Update on the Aging of PBX-9501 via Hydrolysis

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The plastic-bonded explosive PBX-9501, used in weapons, is 94.9% by weight HMX explosive, 2.5% nitroplasticizer (NP), 2.5% Estane® 5703, and 0.1% Irganox 1010 stabilizer (antioxidant). Estane® 5703, made by Noveon, is a poly(ester urethane) random copolymer (Fig. 1) which serves as a glue that binds the HMX crystals together to allow for machining of high precision, high explosive parts. The urethane units segregate (phase separate) into "hard" domains that act as physical crosslinks between the "soft" polyester domains. The NP softens the Estane®, and together this markedly decreases the mechanical sensitivity of the PBX. However, the Estane® slowly degrades in time, and the corresponding effect on the mechanical properties of the PBX raises safety and reliability concerns. Hence, the study of polymer aging is an integral part of the Enhanced Surveillance Campaign.

We are studying the chemical mechanisms of degradation processes in PBX-9501 and developing kinetics models. We are working very closely with a large number of experimentalists at Los Alamos and Pantex to determine the chemical and mechanical properties of the PBX and how the two are related. For degradation of PBX in weapons storage and especially in magazine storage at ambient conditions, hydrolysis of the polyester segments appears to be the dominant mechanism. In this mechanism, a water molecule attacks the soft polyester segment (blue circle in Fig. 1). The resulting chemical reaction cuts the polymer chain in two to produce one polymeric fragment with an alcohol end and another with an acid end. This chain scission process reduces the molecular weight of the Estane® in PBX-9501. As the molecular weight of the Estane® decreases, the mechanical properties of PBX-9501 are affected (such as the ultimate stress and sensitivity to mechanical shock). The hydrolysis mechanism is also reversible. That is, the reverse reaction is also possible in which two polymeric fragments join to produce one longer chain. This re-esterification process or healing of damaged Estane® causes the molecular weight to approach a non-zero equilibrium value for long aging times.

In order to predict the effects of hydrolysis on the molecular weight of Estane® in aged PBX-9501, we fit the theoretical molecular weights computed from a numerical solution of the hydrolysis kinetics equations to four different experimental data sets. The four different aging experiments span a wide range of temperatures and relative humidities (see Fig. 2). The fitting procedure was implemented by simultaneously varying the pre-factors (A_i) and activation energies (E_i) of several chemical rate coefficients [$k_i = A_i \exp(-E_i/RT)$ where T is temperature and R is the gas constant]. The initial values for the chemical rate coefficients were those for pure Estane®

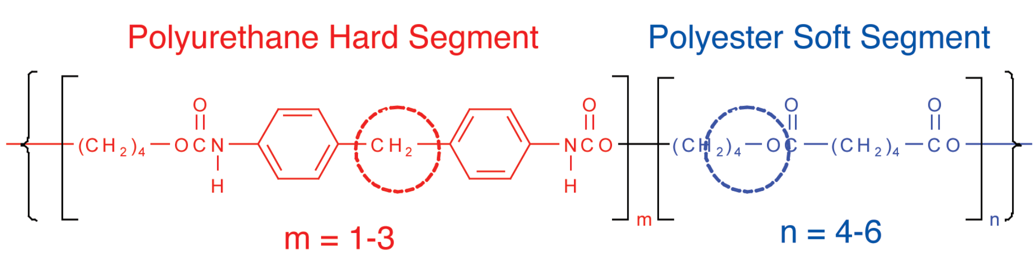

***Fig. 1.* Chemical structure of Estane®.**

which were determined from a previous study [1]. The quality of the fit was determined from the dimensionless root mean square error (DRMSE). The DRMSE was minimized by using a multidimensional simplex fitting algorithm. Once a minimum DRMSE was obtained, the corresponding set of optimal rate coefficients was then used to predict the time evolution of the molecular weight in aged PBX-9501 (see solid curve in Fig. 3).

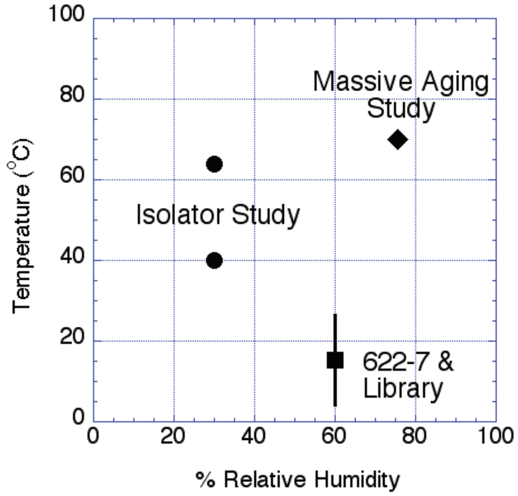

Fig. 2. Aging experiments on PBX-9501.

In conclusion, an optimal set of rate coefficients for the hydrolysis of Estane® in PBX-9501 was obtained. This optimal set of rate coefficients was used to predict the time evolution of the molecular weight in aged PBX-9501. Interesting behavior of the molecular weight as a function of time was observed. The correlation between material properties and molecular weight can be used to make predictions of the material properties as a function of time.

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[1] Salazar, et al., *J. Poly. Sci.: Part A: Poly. Chem.* **41**, 1136–1151 (2003).

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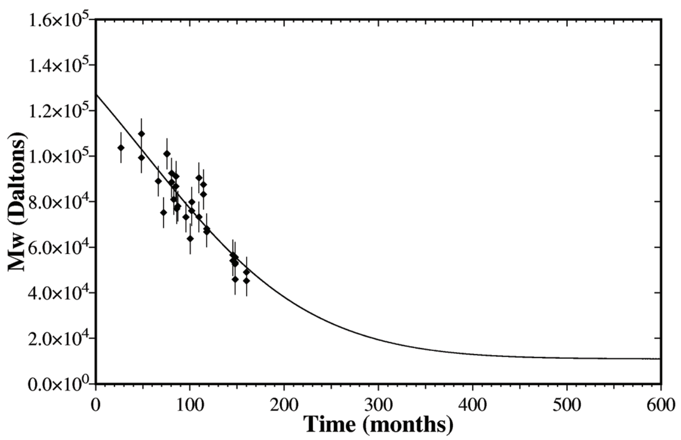

Fig. 3. Molecular weight plotted as a function of time for aged PBX-9501 (solid curve = theory, diamonds = experimental data).